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(54) **Process for decorating objects with enamelled surfaces**

(57) A process for decorating, marking, engraving or the like of objects with enamelled surfaces by means of laser beams, wherein the enamel or enamel raw materials are mixed with turbidity agents which, due to the action of a laser beam, initiate chemical and physical reactions locally and optically and thereby bring about a colour change.

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SPECIFICATION

Process for decorating objects with enamelled surfaces

- 5 The present invention is concerned with a process for the decorating, marking, engraving or the like of objects with enamelled surfaces by means of laser beams.
- 10 More particularly, the present invention is concerned with a process for the decorating, marking, engraving or the like of objects with the use of laser beams which is especially suitable for household objects with an enamelled surface.
- 15 In principle, the decorating and marking of objects by the use of laser beams is known and is used, in particular, in the glass industry and for stainless steel utensils (See German Democratic Republic Patent Specification No. 112,941 and Federal Republic of Germany Patent Specification No. 30 41 072).
- 20 For the achievement of an exact incorporation of decorations and markings or of lettering and for the avoidance of damage to neighbouring surfaces, various processes of carrying out have been developed, especially for the decoration of glass and ceramic articles. These concern, on the one hand, chronological changes of the irradiation capacity and thus of the energy action on the objects. On the other hand, it is known temporarily to apply a
- 25 protective layer for the prevention of damage to the surface during the irradiation. For the avoidance of damage, it has also been suggested to allow a protective cooling medium to act during the irradiation (see German Democratic Republic Patent Specifications Nos. 118,251 and 212,701).
- 30 However, the application of these known process steps to the decoration, marking, engraving and the like of objects coated with an enamelled layer is only limited and is only possible with additional complicated and laborious measures, whereby, however,
- 35 the appearance satisfying all requirements cannot be achieved. In particular, it is not possible to achieve, with the known processes, decorations in the stoving-in process in the case of one-layer direct
- 40 enamelling. Furthermore, such decorations and markings are, in the case of comparatively long usage of the objects in question, doubtfully hygienic (bubble structure of the enamel layer).
- 45 By means of the process according to the present invention, it is possible to use a laser radiation for the decorating, marking, engraving and the like of objects with an enamelled surface layer and, with only a small expense, to ensure an optically satisfactory recognisability of the radiated-in decoration,
- 50 marking or lettering without the danger of damaging the adjoining surfaces or without the possibility of the objects becoming unhygienic in the course of use.
- 55 Thus, it is an object of the present invention to provide a process with which, with the use of laser devices, there are provided the prerequisites for the working of enamelled objects and for the achievement of a satisfactory appearance of the decorations, engravings, markings, letterings and the like.
- 60 Thus, according to the present invention there is

provided a process for decorating, marking, engraving or the like of objects with enamelled surfaces by means of laser beams, wherein the enamel or enamel raw materials are mixed with turbidity agents, such as oxides of titanium, tin, cerium or antimony, which, due to the action of a laser beam, initiate chemical and physical reactions locally and optically and thereby bring about a colour change.

- The irradiation can be carried out in the case of
- 75 enamel surface layers which have already been stoved in, as well as in the case of non-stoved enamel coatings and also in the case of still hot and plastic enamel layers. According to a further feature of the present invention, the edges resulting due to the laser irradiation can be melted by the further action of a laser beam with a different energy action or by heating the whole object by means of known sources of heat. For the further improvement of the total effect obtained, according to requirements,
- 80 there can be carried out a further treatment by coating with another enamel layer. This layer can thereby consist of transparent, cloudy, non-cloudy or coloured enamel. According to a further feature of the present invention, during the laser irradiation, the surfaces can be additionally covered over by absorbent material impregnated with fluxes, lustres or strongly colouring salt solution by means of which the appearance effect can be additionally positively influenced.
- 85 These process steps can be used not only for a laser treatment in the case of enamel layers applied by conventional processes but also in the case of objects treated directly or treated by a two-layer stoving-in process.
- 90 The following Examples are given for the purpose of illustrating the present invention.

Example

- 105 A utensil made of aluminium is pretreated in conventional manner and subsequently sprayed with an enamel paint, the enamel paint used having one of the following compositions:

- a) 100 parts by weight of frit
110 15 parts by weight of titanium dioxide
15 parts by weight of adjusting agent
40 parts by weight of water
- b) 100 parts by weight of frit
5 parts by weight of coloured bodies
115 5 parts by weight of titanium dioxide
15 parts by weight of adjusting agent
40 parts by weight of water.

- After spraying on the enamel paint, there follows a stoving in of the enamel. The finished, stoved article is now subjected to the action of a laser decorating device. According to a predetermined programme, by means of a carbon dioxide laser beam, there is applied a decoration to the utensil in that the admixed turbidity agent (titanium dioxide) is dissolved locally or optically according to the guiding of the laser beam.

Example 2

- 120 The control knob cover of a gas or electric stove is

to be marked with the markings of the manufacturer, as well as with operating instructions. According to the present invention, this takes place in the following way:

- 5 The basic enamelling is first carried out in conventional manner. Subsequently, by spraying, there is applied a covering enamel which contains 20% of melted-in titanium dioxide. After drying, there then follows the desired lettering of the object with a
10 carbon dioxide or YAG laser according to a predetermined programme. Thereafter, there is carried out the stoving-in of the object at a stoving temperature usual for the enamel.

15 *Example 3*

- A sheet steel utensil is base and cover enamelled in a conventional manner, the covering enamel thereby containing a turbidity agent according to the present invention. The enamelled object is then
20 decorated by means of a laser beam in the manner already described in Examples 1 and 2. On to the decorated object is now applied a coloured, transparent enamel in the form of a majolica enamel which is then dried and stoved. There is thereby obtained
25 an enamelled utensil with a beautiful decoration in which the contours imparted by the laser beam appear through the majolica enamel.

CLAIMS

- 30 1. Process for decorating, marking, engraving or the like of objects with enamelled surfaces by means of laser beams, wherein the enamel or enamel raw materials are mixed with turbidity agents which, due
35 to the action of a laser beam, initiate chemical and physical reactions locally and optically and thereby bring about a colour change.
2. Process according to claim 1, wherein the turbidity agent is an oxide of titanium, tin, cerium or
40 antimony.
3. Process according to claim 1 or 2, wherein the irradiation is carried out by means of a laser either in the case of stoved-in or in the case of non-stoved enamel surface layers.
- 45 4. Process according to claim 1 or 2, wherein the irradiation is carried out when the enamel surface is still hot or plastic.
5. Process according to any of the preceding claims, wherein the surface treated by the laser or
50 the whole of the object is subjected to a further heat treatment.
6. Process according to any of the preceding claims, wherein the surface of the object treated by means of a laser is provided with a further layer of
55 transparent, cloudy, non-cloudy or coloured enamel.
7. Process according to any of the preceding claims, wherein the surface is covered during the laser irradiation by an absorbent material which is impregnated with a flux, lustre or strongly colouring
60 salt solution.
8. Process according to claim 1 for decorating, marking, engraving or the like of objects with enamelled surfaces, substantially as hereinbefore described and exemplified.
- 65 9. Objects which have been decorated, marked,

engraved or the like by the process according to any of claims 1 to 8.

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